PB86-119088

Fly Ash Recycle in Dry Scrubbing

Texas Univ. at Austin

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Oct 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-119088

EPA/600/D-85/257
October 1985

FLY ASH RECYCLE IN DRY SCRUBBING

by

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EPA Cooperative Agreement
CR811531

EPA Project Officer
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Air and Energy Engineering Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/D-85/257	2.	3. RECIPIENT'S ACCESSION NO. PB86 119087AS
4. TITLE AND SUBTITLE Fly Ash Recycle in Dry Scrubbing		5. REPORT DATE October 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Wojciech Jozewicz and Gary T. Rochelle		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of Texas at Austin Department of Chemical Engineering Austin, Texas 78712		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. CR811531
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Published Paper; 14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES AEERL project officer is Theodore G. Brna, Mail Drop 61, 919/541-2683.		

16. ABSTRACT The paper describes effects of fly ash recycle in dry scrubbing. (Previous workers have shown that the recycle of product solids improves the utilization of slaked lime--Ca(OH)2--for sulfur dioxide (SO2) removal by spray dryers with bag filters.) In laboratory-scale experiments with a packed-bed reactor, utilization was increased several-fold when the Ca(OH)2 was first slurried with one of several different fly ashes. The enhancement increased with the higher loading of fly ash--g fly ash/g Ca(OH)2. Much higher Ca(OH)2 utilization was achieved when silicic acid was used instead of fly ash. Scanning electron microscopy supports the explanation that Ca(OH)2 and silica dissolve and reprecipitate as a more reactive calcium silicate. Other major constituents of fly ash have less or no effect at all on Ca(OH)2 utilization. The amount of calcium in the fly ash did not affect the overall SO2 removal after Ca(OH)2 was added. Slurrying for longer than 2 hours at higher than 60 C can improve the utilization of Ca(OH)2 slurried with fly ash.

17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Slurries	Pollution Control	13B 11G
Scrubbers	Inorganic Silicates	Stationary Sources	07A, 13I
Fly Ash	Calcium Silicates	Dry Scrubbing	21B
Circulation		Recycling	14G
Sulfur Dioxide		Slaked Lime	07B
Calcium Oxides		Silicic Acid	
Spray Drying			13H
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 30
		20. SECURITY CLASS (This page) Unclassified	22. PRICE $9.95

EPA Form 2220-1 (9-73)

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Abstract

Previous workers have shown that the recycle of product solids improves the utilization of slaked lime [$Ca(OH)_2$] for SO_2 removal by spray dryers with bag filters. In laboratory-scale experiments with a packed bed reactor, utilization was increased several-fold when the $Ca(OH)_2$ was first slurried with one of several different fly ashes. The enhancement increased with the higher loading of fly ash [g fly ash/g $Ca(OH)_2$]. Much higher $Ca(OH)_2$ utilization was achieved when silicic acid was used instead of fly ash. Scanning electron microscopy supports the explanation that $Ca(OH)_2$ and silica dissolve and reprecipitate as a more reactive calcium silicate. Other major constituents of fly ash have less or no effect at all on $Ca(OH)_2$ utilization. The amount of calcium in the fly ash did not affect the overall SO_2 removal after $Ca(OH)_2$ was added. Slurrying for longer than 2 hours at higher than 60°C can improve the utilization of $Ca(OH)_2$ slurried with fly ash.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Flue gas desulfurization by the means of spray dryer and bag filter is an important new alternative to limestone slurry scrubbing. In the spray dryer/bag filter system, flue gas is contacted with a fine spray of an aqueous solution or slurry of a reactive alkali [typically $Ca(OH)_2$]: SO_2 removal and drying occur simultaneously. Since not all moisture is removed from the solids in the spray dryer, the remaining moisture promotes further removal of SO_2 in the duct joining the spray dryer and bag filter and in the bag filter itself. Therefore the total SO_2 removal in the system is a sum of removal in the spray dryer, the connecting duct, and bag filter.

Advantages of spray drying over the conventional slurry scrubbing methods are production of a dry solid waste and equipment construction from carbon steel. Economic studies have indicated that, for low and medium sulfur coals, dry scrubbing systems should compete economically with wet systems [1 - 3]. Numerous authors report that recycle of product solids and fly ash in $Ca(OH)_2$ spray dryer scrubbing results in substantial improvement of reagent utilization and SO_2 removal [4 - 7]. A spray dryer model based on gas/film mass transfer to liquid droplet overpredicts the performance of actual systems without recycle, but underpredicts the performance of the systems in which the recycle was used [8]. This suggests that there must be a substantial effect of gas/solid reactions enhanced by fly ash recycle. This paper explains this effect by studying the reaction of SO_2 with mixtures of $Ca(OH)_2$/fly ash, $Ca(OH)_2/SiO_2$, and $Ca(OH)_2/Al_2O_3$ at bag filter concitions.

FLY ASH RECYCLE IN PILOT PLANTS

Solids recycle from the spray dryer has been used to obtain better utilization of $Ca(OH)_2$. This option provides a higher $Ca(OH)_2$ concentration in the slurry feed at the same $Ca(OH)_2$ stoichiometric ratio [moles of $Ca(OH)_2$ fed to the system/moles of SO_2 in the feed gas]. In one pilot plant, increasing the recycle ratio [g solids recycled/g fresh $Ca(OH)_2$] from 6:1 to 12:1 increased SO_2 removal in the spray dryer from 70 to 80% at a stoichiometry of 1.0 [9]. In another installation, compared to once-through lime tests, recycle tests gave 10 to 15% more SO_2 removal at a stoichiometry of 1.5 [10].

Another option enhancing lime utilization uses the recycle of both solids collected in the spray dryer and solids from the baghouse. However, removal was not significantly different employing either spray dryer solids or fabric filter solids as a recycled material [11]. At a stoichiometry of 1.0 the removal increased from 53% when no recycle was employed to 62% with 0.5:1 recycle ratio. When ash content in the feed slurry increased from 5 to 20%, SO_2 removal in the spray dryer increased from 80 to 92% for a stoichiometry of 1.6 [10].

A/S Niro Atomizer ran several experiments investigating the effects of fly ash recycle and proved it to be beneficial for SO_2 removal in a spray dryer [12]. According to their results, substantially higher removal of SO_2 may be achieved when recycling the fly ash and $Ca(OH)_2$ than when recycling $Ca(OH)_2$

alone. Corresponding efficiencies for a stoichiometry of 1.4, 500 ppm inlet SO_2, and comparable solids concentration were 84 and 76%, respectively. For the same stoichiometry and SO_2 concentration, removal was only 67% for the simple once-through process. At low SO_2 concentration and high recycle ratios, over 90% removal was achieved even at extremely low stoichiometry. At 548 ppm SO_2, 25:1 recycle, 0.76 stoichiometry and at 170 ppm SO_2, 110:1 recycle, 0.39 stoichiometry, SO_2 removal was 93.8 and 97.8%, respectively.

Removal efficiencies up to 65% were reported with a slurry of highly alkaline (20% CaO) fly ash only [13]. In another experiment, 25% SO_2 removal was achieved when spraying slurried fly ash collected from a boiler burning 3.1% sulfur coal [14]. A weak trend found in a study of 22 samples of fly ash was that a slurry with a higher total slurry alkalinity tended to have a higher SO_2 capture [15]. A potentially significant hypothesis has been presented, which claimed that the fraction of available alkalinity which was utilized during a single pass through the scrubber was diminished as the alkalinity increased [16].

The results presented above show that there must be a substantial reaction between recycled $Ca(OH)_2$ and fly ash, promoting SO_2 removal in a spray dryer. The formation of hydrated calcium silicates during the recycle and their subsequent reaction with SO_2 may be the possible explanation of this phenomenon.

$CaO - SiO_2 - Al_2O_3 - H_2O$ System

The nature of calcium silicate hydrate, calcium aluminate hydrate, and calcium aluminate silicate hydrate formation in $CaO - SiO_2 - Al_2O_3 - H_2O$ systems is very complicated. It is usually impossible to assign a simple chemical formula to these products, especially at ordinary temperatures of interest in flue gas desulfurization [17]. At temperatures from 20 to about 100°C, two main calcium silicate hydrates are formed. Their ratio depends on the initial ratio of calcium to silica in the slurry [18]. Both monocalcium silicate hydrate [$CaO \times SiO_2 \times H_2O$] and dicalcium silicate hydrate [$(CaO)_2 \times SiO_2 \times H_2O$] are fibrous gels of specific surface areas in the range of 100-300 m^2/g [19]. At 20 - 100°C after 8 hours of hydration, tobermorites (calcium silicate hydrates) may crystallize which are of high surface area [20]. However, below 100°C reactions yielding calcium silicate hydrate normally give poorly crystallized materials [17].

The reaction of fly ash and $Ca(OH)_2$ in the presence of water is called the pozzolanic reaction. A pozzolan is a siliceous or siliceous and aluminous material which in itself possesses little or no cementitous value but will, in finely divided form and in the presence of moisture, chemically react with $Ca(OH)_2$ at ordinary temperatures to form compounds possessing cementitous properties [21]. Due to small particle size and generally noncrystalline character, fly ash usually shows pozzolanic properties, or pozzolanic and cementitous properties in the case of high-calcium ashes [22]. High-calcium fly ash contains tricalcium aluminate hydrate, which is the most reactive

mineral present in portland cement [23]. Pozzolanic reactions give products with cementitous properties and high surface areas that can enhance SO_2 removal.

During fly ash recycle in dry flue gas desulfurization systems, reaction of fly ash with makeup $Ca(OH)_2$ or unreacted, recycled $Ca(OH)_2$ probably takes place in several steps. First, $Ca(OH)_2$ dissolves in water. Then silica and alumina are digested from the fly ash. Finally calcium aluminum silicate hydrates are formed and reprecipitate on the surface of the fly ash.

EXPERIMENTAL

Apparatus

Experiments were conducted in the apparatus [24] shown in Figure 1. The glass reactor (40 mm in diameter, 120 mm in height) was packed with a powdered reagent mixed with 40 g of 100 mesh silica sand to prevent channelling of $Ca(OH)_2$ [25]. The reactor was immersed in a water bath controlled by a thermostat to within 0.1°C. Simulated flue gas was obtained by mixing nitrogen and sulfur dioxide from gas cylinders. The flow of gas was monitored using rotameters. Water was metered by a syringe pump, evaporated, and injected into the dry gas. Reactor tubing upstream of the water injection was heated to prevent condensation of the moisture.

Before entering the analyzer, the gas was cooled and water condensed by an ice bath. The SO_2 concentration was measured with a pulsed fluorescent SO_2 analyzer (ThermoElectron Model 40). A bypass of the reactor allowed preconditioning of the bed and stabilization of gas flow at the desired SO_2 concentration. Prior to each run the bed was humidified by pure nitrogen at a relative humidity of about 98% for 6 minutes and then pure nitrogen at a relative humidity at which the experiment was to be performed for 10 minutes.

Most of the experiments were performed at a relative humidity of 54% with some experiments at 17 and 74%. At typical flue gas conditions, 17, 54, and 74% relative humidities correspond to 38, 9.5, and 4.7°C approaches to saturation, respectively. Reactor temperatures were 95, 66, and 64.4°C for 17, 54, and 74% relative humidities, respectively. Common purity (99.5%) nitrogen at 4.6 l/min (0°C, 1 atm) was used as a carrier gas. The nominal concentration of SO_2 was 500 ppm, and exposure time of the sample to the sulfurized gas was 1 hour.

Sample Preparation

The sample preparation consisted of two essential steps: slurrying and drying. In every experiment 0.4 g of reagent grade $Ca(OH)_2$ was used. This amount of $Ca(OH)_2$ was slurried with fly ash or other additive at the desired loading. The water-to-solids ratio was between 10:1 and 20:1, most often 15:1. A propeller stirrer at 350 rpm was used to agitate the slurry. Slurrying time varied from 2 to 24 hours, and the temperature of the slurry

was set at 25 to 92°C. The samples used for the investigation of the effect of slurrying conditions were vacuum filtered (about 5 min) and subsequently vacuum dried (about 10 min) at 95°C. All other samples were dried overnight in an atmospheric oven without filtering; it took several hours to evaporate the water. The new drying procedure (vacuum filter and oven) was introduced to minimize the additional reaction time of a wet sample in high oven temperature (85-90°C).

Sample Characterization

Four different fly ashes were slurried with $Ca(OH)_2$. The characterization of the fly ashes is given in Table 1. During the experiments on slurrying conditions, a new batch of fly ash IV was used. It was obtained from the same vendor and was produced by burning coal from, reportedly, the same source. These samples were characterized by scanning electron microscopy (SEM). The composition of the particles was found using a Kevex Micro-X 7000 X-ray Energy Spectrometer (XES). Mean particle size was determined using a Hiac-Royco particle counter.

RESULTS

The Effect of Fly Ash Type and Ratio

Four samples of fly ash were slurried with $Ca(OH)_2$ at a loading of 4 [4 g fly ash/g $Ca(OH)_2$] for 4 hours at 65°C and reacted at a relative humidity

of 54% (54% RH). The samples having the best and the worst performance at 54% RH were also tested at the extreme humidities of 17 and 74%. The results are presented in Figure 2. Also shown in Figure 2 are the conversions when $Ca(OH)_2$ only was exposed to the sulfurized gas. With 0.4 g $Ca(OH)_2$ the average SO_2 removal would be 83% with 100% utilization of $Ca(OH)_2$. As can be seen, all fly ashes improved the utilization at every RH investigated. Samples with 16 g fly ash/g $Ca(OH)_2$ (slurried at the same conditions as above) enhanced utilization at 54% RH to a greater extent than was the case for 4 g fly ash/g $Ca(OH)_2$. The $Ca(OH)_2$ utilization was 67, 79, 65, and 71% when fly ashes I, II, III, and IV were used, respectively. These values are much higher than the ones presented in Figure 2. Based on these two series of experiments, no correlation was found between SO_2 removed and calcium content of the fly ash sample.

Fly ash I was selected to test the effect of fly ash loading on $Ca(OH)_2$ utilization. The results of experiments at 54% RH are presented in Figure 3. Increasing fly ash loading from 0.5 to 20 g/g $Ca(OH)_2$ increased $Ca(OH)_2$ utilization from 17 to 78%.

Additives Other Than Fly Ash

The other main components of fly ash were also investigated. Reagent grade Al_2O_3, Fe_2O_3, and silicic acid were used as sources of alumina, iron, and silica, respectively. Fly ash was simulated as a mixture of three substances: 49% H_2SiO_3, 29% Al_2O_3, and 22% Fe_2O_3 (weight %). Figure 4 shows that

this mixture models the performance of fly ash at a loading of 4 (30 and 27%, respectively). This again implies that calcium content of fly ash is not of primary importance, since the utilization of added $Ca(OH)_2$ was higher when no fly-ash-bound calcium was present.

The addition of silicic acid had the most significant effect on the $Ca(OH)_2$ utilization. No SO_2 removal was observed when silicic acid alone was exposed to simulated flue gas. Figure 5 gives the effect of silica loading on conversion at 17 and 54% RH. Silicic acid was used for most of these experiments. Some experiments were performed with Zeothix 265 and Zeofree 80, synthetic precipitated silicas of surface area 250 m^2/g and 140 m^2/g, respectively (samples and data obtained courtesy of Huber Corp.). However, these substances did not enhance $Ca(OH)_2$ utilization significantly better than silicic acid (Figure 5). As can be seen from Figure 5, $Ca(OH)_2$ conversion increased with silicic acid loading. The comparison of the results presented in Figures 3 and 5 shows that silicic acid promotes $Ca(OH)_2$ utilization better than fly ash. For example, at 54% RH and 8 g silicic acid/g $Ca(OH)_2$, the conversion of lime was 78%. At 8 g fly ash I/g $Ca(OH)_2$, the conversion was 65%.

Reactivities of fly ash and silicic acid should be compared on the basis of silica content. Assuming that fly ash I is 50% silica, 8 g silicic acid/g $Ca(OH)_2$ should be compared to 16 g fly ash I/g $Ca(OH)_2$ (conversions of 78 and 68%, respectively). The difference between silicic acid and fly ash is more

apparent at lower loadings. For 1 g silicic acid/g $Ca(OH)_2$, conversion was 53%, and for 2 g fly ash I/g $Ca(OH)_2$, it was 32%.

The effect of alumina loading was tested at 54% RH using two sources of alumina (Figure 6). When reagent grade Al_2O_3 was used, increasing loading did not change SO_2 removal. No SO_2 removal was observed for Al_2O_3 alone. However, the removal increased with increasing loading of activated alumina (chromatographic grade, 80-200 mesh). Activated alumina alone removed SO_2. The adsorptive capacity of activated alumina was calculated as 0.023 g of SO_2 per g of alumina. Based on this value, the corrected SO_2 removal has been determined due to the possible formation of calcium aluminates. These corrected values are lower than the ones observed for the same additive loading when silicic acid was used instead of alumina. Therefore, the silica content of fly ash is mainly responsible for the enhancement of $Ca(OH)_2$ utilization.

Slurrying Conditions

Slurrying tests were performed at 25, 45, 55, 65, and 92°C, and time was varied from 2 to 24 hours. The samples for these test were prepared by vacuum filtration and vacuum drying. Both old and new batches of fly ash IV were used as a source of silica at 16 g fly ash/g $Ca(OH)_2$. Reactor relative humidity during exposure was 54%. $Ca(OH)_2$ conversion is given in Figure 7.

As can be seen, the slurrying temperature was the decisive parameter affecting the process. The results show that there is a critical slurrying

time for every temperature tested, for which $Ca(OH)_2$ conversion reaches a maximum value. The time needed to reach this maximum shortens with increasing temperature. $Ca(OH)_2$ conversion converged on 40% after 16 hours of slurrying at 25°C and 80% after 5 hours at 92°C. Compared with 12% utilization of $Ca(OH)_2$ alone at 54% RH, the utilization of fly ash/$Ca(OH)_2$ slurried at 65°C improved dramatically.

SEM photographs (Figures 8 and 9) show the development of the surface area of the samples. Figure 8 shows the sample slurried for zero time. Separate fly ash spheres with smooth surfaces (as in an unslurried fly ash) and irregular particles of $Ca(OH)_2$ can be seen. Increasing the temperature of slurrying to 92°C resulted in a well developed surface area of the deposit as depicted in Figure 9.

The maximum utilization of $Ca(OH)_2$ is not a uniform function of the temperature of slurrying (40, 50, 55, 80, and 80% for 25, 45, 55, 65, and 92°C, respectively). There appears to be a discontinuity between 55 and 65°C that may indicate a change in the hydration of the calcium aluminum silicate. The resulting solids have better reactivity for SO_2 removal than those formed below 55°C. When tested by Differential Scanning Calorimetry (DSC), the solids formed at 65 and 92°C have an additional endothermic peak between 416 and 465K (143 and 192°C). No peak was observed for samples slurried at 25, 45, and 55°C. The DSC scans of the samples of 16 g fly ash IV/g $Ca(OH)_2$ slurried at 65 and 55°C are shown in Figures 10 and 11, respectively.

CONCLUSIONS

1. Enhanced performance of spray dryer/bag filter systems with recycle of fly ash and calcium solids is probably due to reaction of $Ca(OH)_2$ with fly ash to produce calcium silicates. The calcium silicate solids have greater surface area than the unreacted $Ca(OH)_2$ and are more effective for gas/solid reactions.

2. Calcium silicates are more reactive than aluminates or ferrites. The available silica content of the fly ash is most important.

3. Increased time and temperature give more reactive solids from the reaction of lime and fly ash. Solids formed above 65°C are substantially more reactive than solids formed at lower temperature.

ACKNOWLEDGEMENTS

This work was performed under EPA Cooperative Agreement CR-811531. The EPA project officer was Theodore G. Brna.

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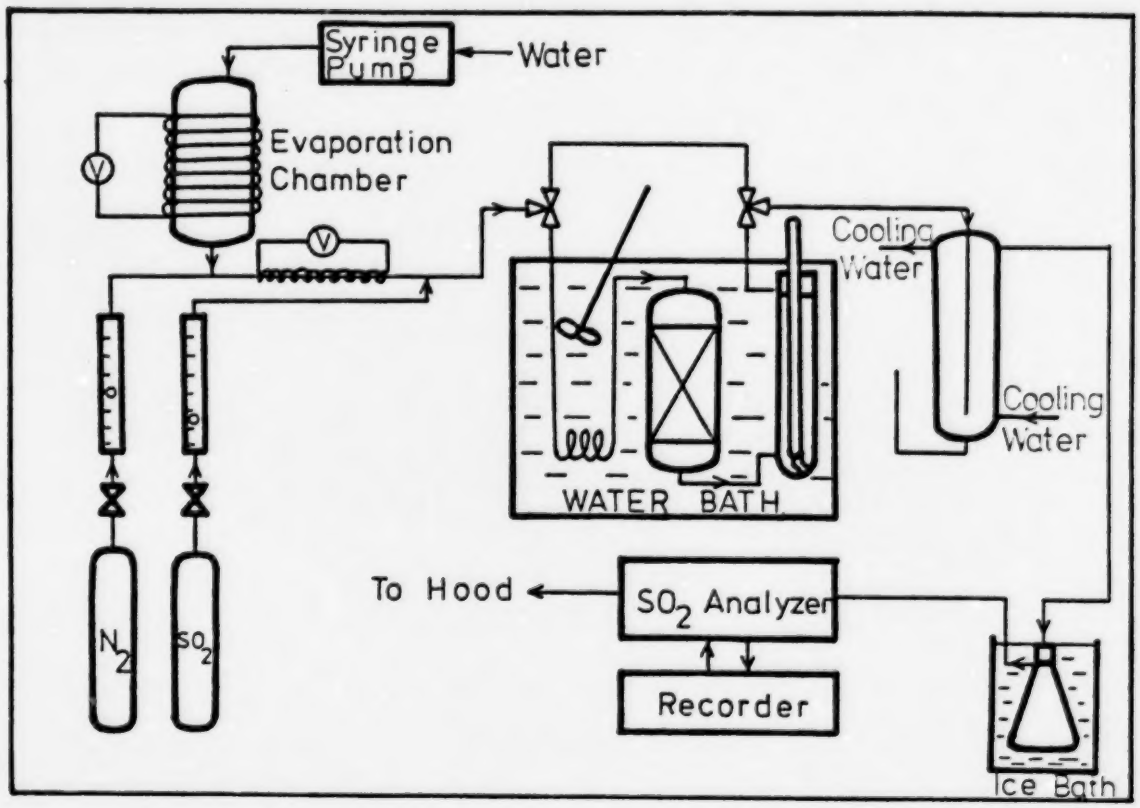

Figure 1. Experimental apparatus.

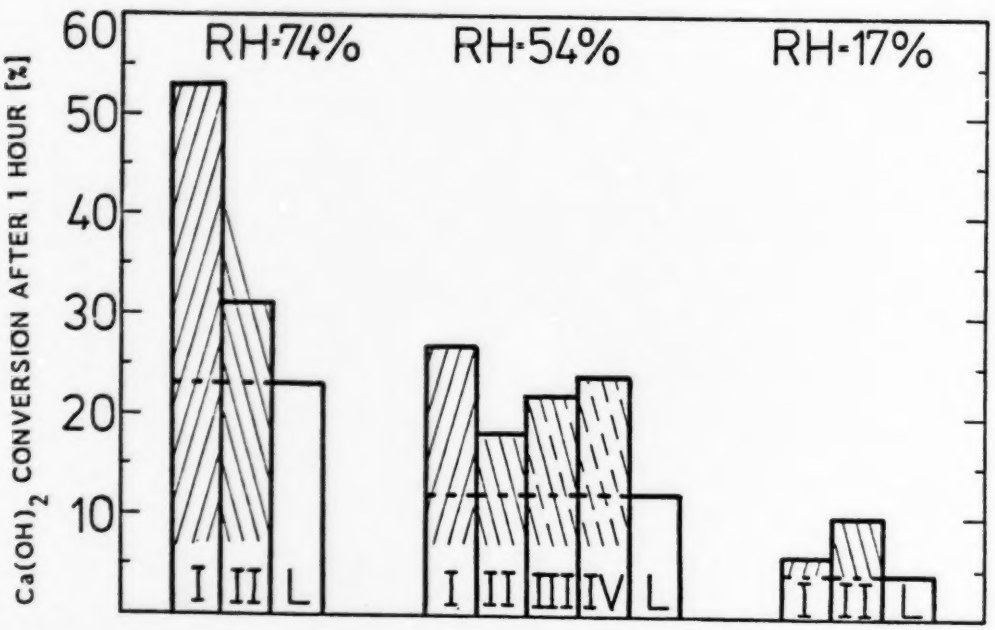

Figure 2. The effect of fly ashes I, II, III, and IV and relative humidity on $Ca(OH)_2$ utilization, L = $Ca(OH)_2$ alone.

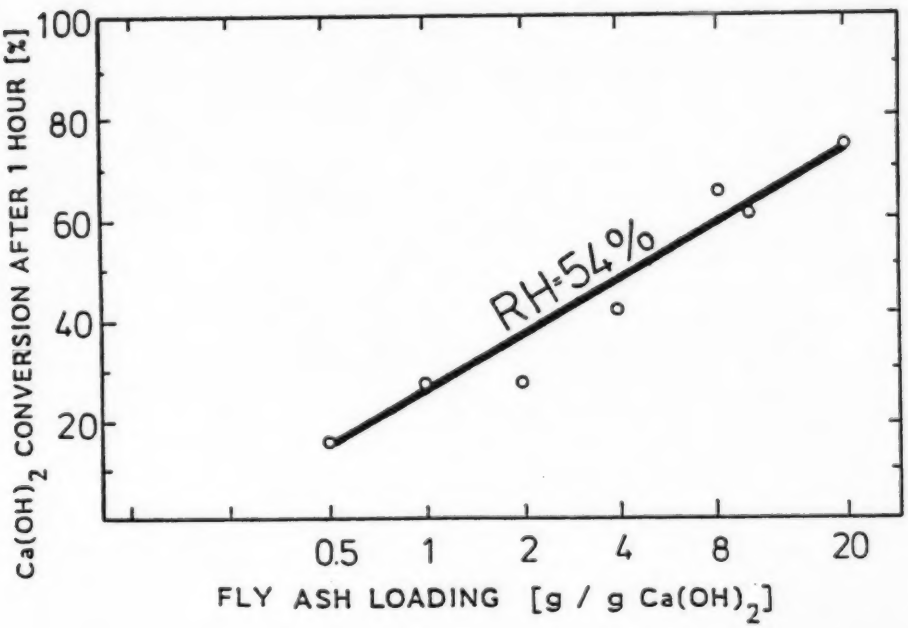

Figure 3. The effect of fly ash I loading on $Ca(OH)_2$ utilization.

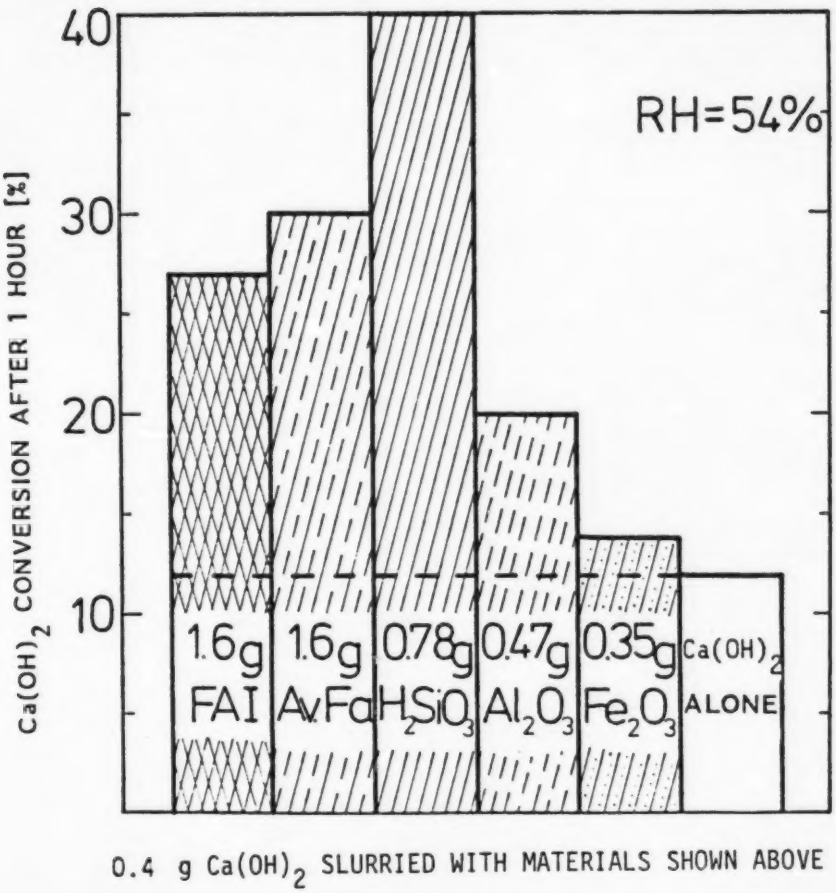

Figure 4. The fly ash simulation experiment at 54% RH. Simulated fly ash (Av.Fa.) and reagent grade mixtures slurried with 0.4 g of $Ca(OH)_2$ for 4 hours at 65°C.

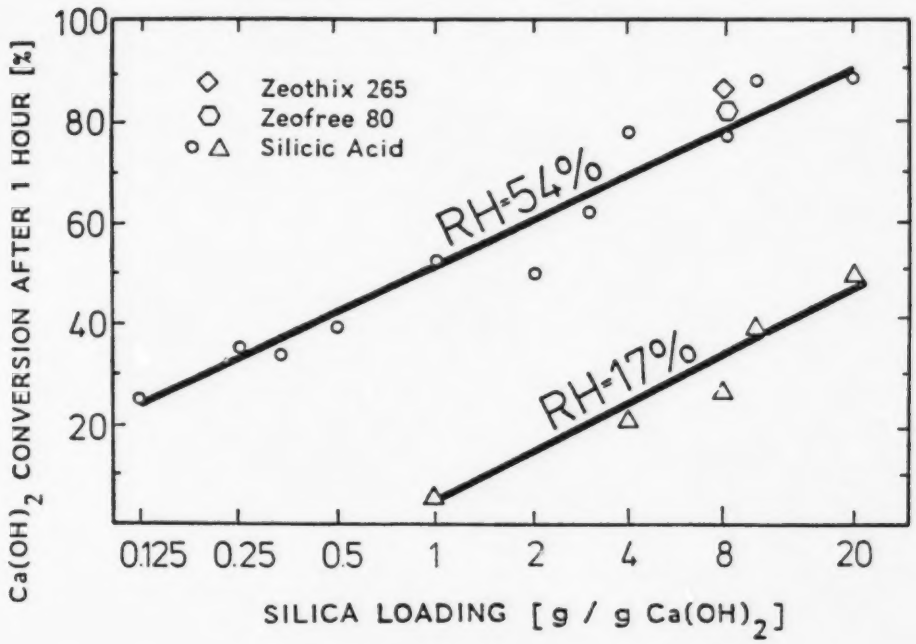

Figure 5. The effect of silica loading on $Ca(OH)_2$ utilization.

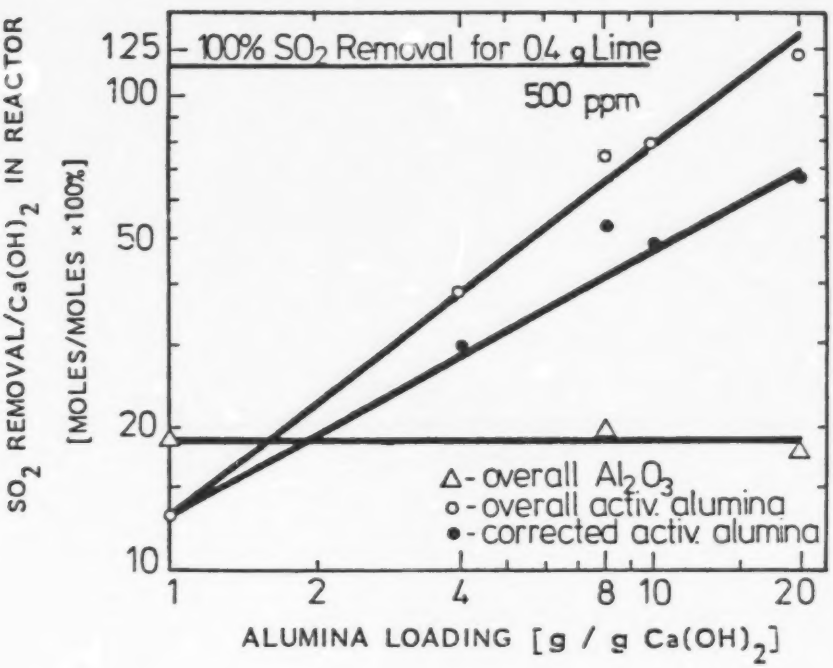

Figure 6. The effect of alumina loading on $Ca(OH)_2$ utilization at 54% RH and at SO_2 concentration of 500 ppm.

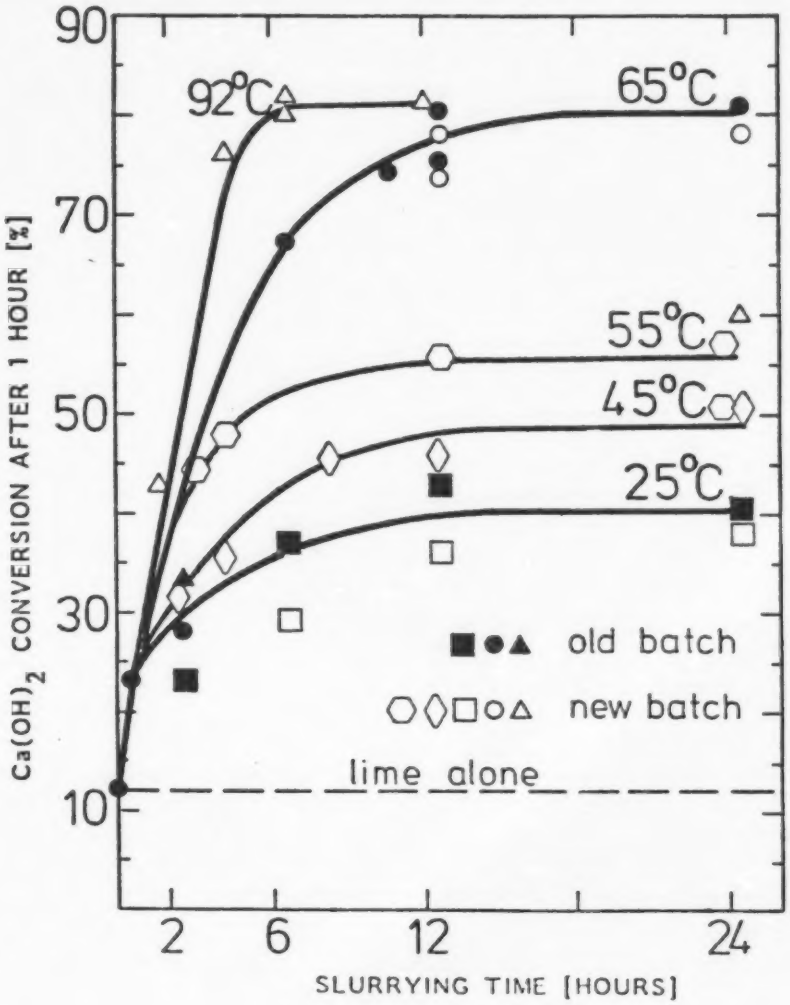

Figure 7. The effect of fly ash IV on $Ca(OH)_2$ reactivity, 16 g fly ash IV/g $Ca(OH)_2$.

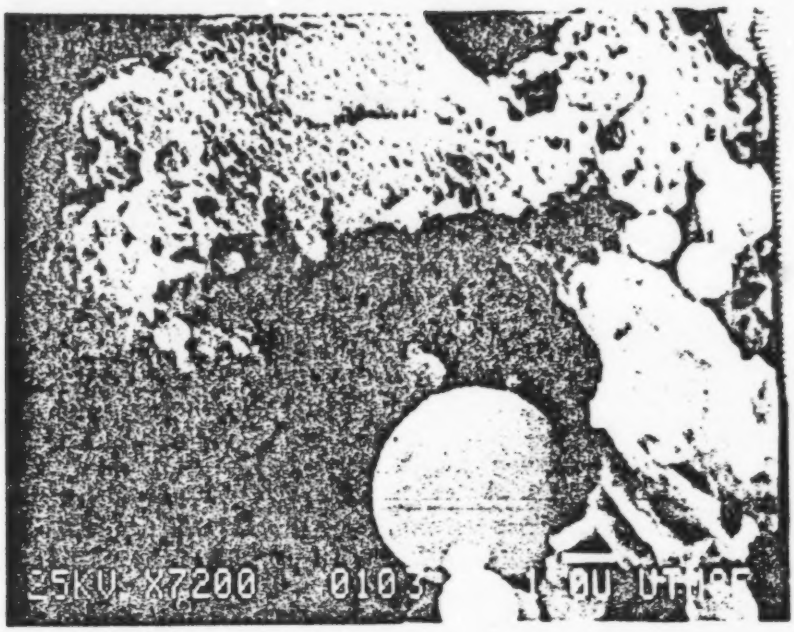

Figure 8. SEM photograph of 16 g fly ash IV/g $Ca(OH)_2$ sample slurried for zero hours.

Figure 9. SEM photograph of 16 g fly ash IV/g $Ca(OH)_2$ sample slurried for 12 hours at 92°C.

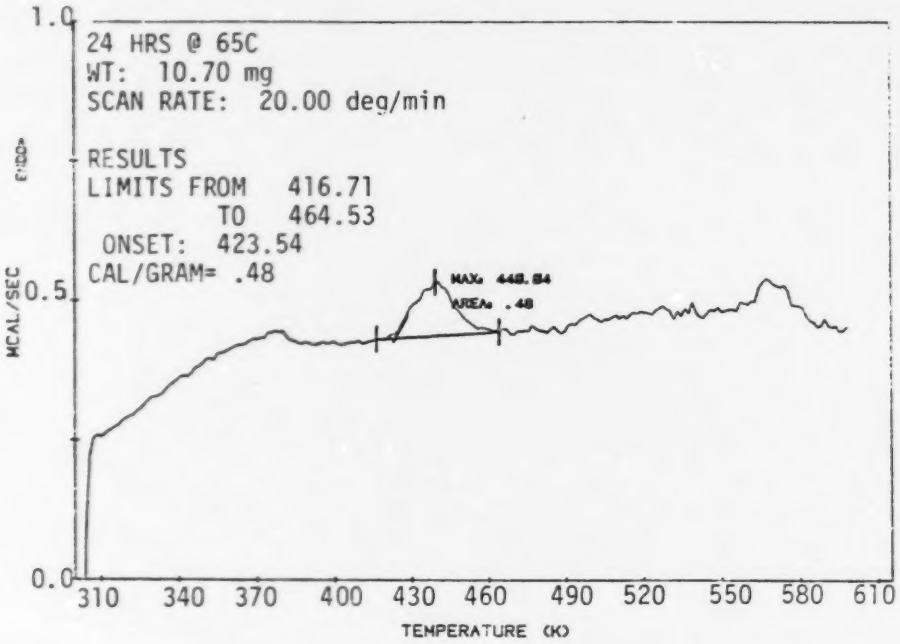

Figure 10. DSC scan of a sample of 16 g fly ash IV/g $Ca(OH)_2$ slurried for 24 hours at 65°C.

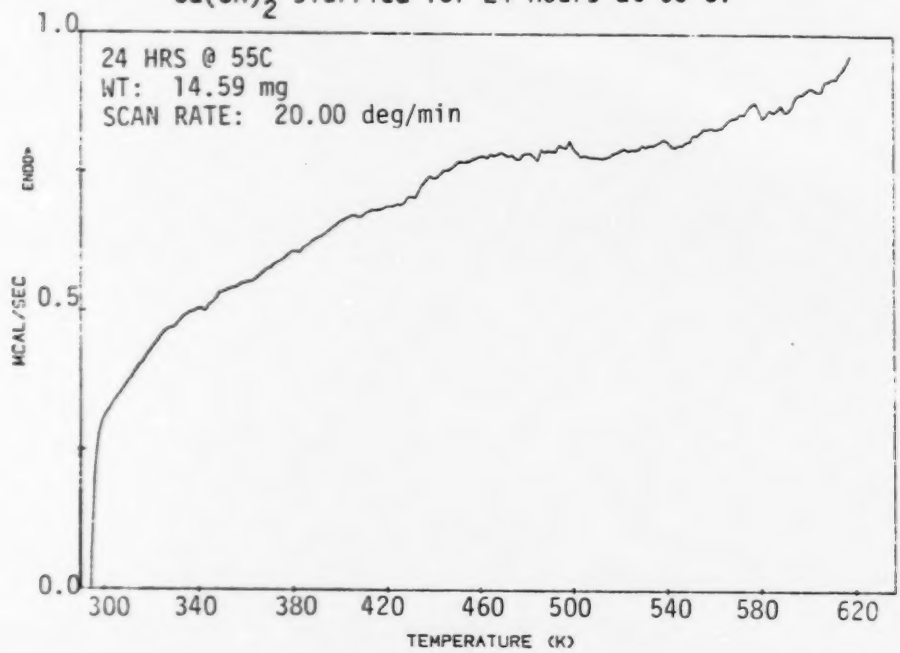

Figure 11. DSC scan of a sample of 16 g fly ash IV/g $Ca(OH)_2$ slurried for 24 hours at 55°C.

Table 1. Fly Ash Characterization.

Fly Ash	I	II	III	IV	
Power Plant	Bull Run Plant TVA	Gibson Plant Public Service of Indiana	Seminole Electric Coop. Palatka, FL	San Miguel Electric Coop. San Miguel, TX	
Coal Type	bituminous	bituminous	bituminous	lignite	
XES Analysis [weight %]					
Ca	34	5	4	11[a]	15[b]
Si	42	41	59	66	68
Fe	6	31	15	4	2
Al	16	20	20	18	14
Mass Mean Particle Size [μm]	19	9	14	10	10

[a] Old Batch

[b] New Batch